COMMENTS ON THE COMPOSITION OF CATLINITE AND OHIO PIPESTONE

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Recent articles by Holzapfel (1995) and Britt (1995) indicate a continuing interest in these two raw materials. Holzapfel provides information derived primarily from Stout (1923) and presents it in the context of a recent expedition made to obtain a representative sample of Ohio pipestone, which she correctly identifies as a Pennsylvanian fireclay known geologically as Sciotoville clay. Britt is more specifically interested in distinguishing the Ohio and Minnesota "pipestones," particularly in terms of chemical composition, and it is to this end that the following comments are directed, as a number of pertinent publications, including Stout (1923) were apparently not available to him.

The original "1836" chemical analysis of catlinite by Prof. C.T. Jackson and provided Britt by a "lady ranger" at Pipestone National Monument was actually published in the *American Journal of Science* (Anonymous 1839). Jackson regarded the rock as a new compound very similar to "agalmatolite," a stone used for carving in China, and named the new rock "catlinite" in honor of George Catlin.

By 1884, similar deposits had been recognized and identified as catlinite at various places in Minnesota, Wisconsin (e.g., Devil's Lake), and South Dakota, also in association with Algonkian quartzites, as is the case in Minnesota, where the catlinite occurs as thin layers interbedded with the Precambrian Sioux quartzite, exposed along a north-south-trending ridge about a mile in length and 25-30 feet in height (Broughton 1973). Winchell (1884: 63) provided additional chemical analyses of the Minnesota stone, as well as similar material from South Dakota and Wisconsin. He noted that the Minnesota pipestone "seems to graduate into red shale, and becomes in that form an important constituent of the formation in which it is found. It seems to be only when this formation is greatly indurated that the inclosed shale beds are hardened to the condition of pipestone. In cases of greater metamorphism its heaviest deposits have been converted apparently into red felsite or quartz porphyries."

The next available analysis of Minnesota catlinite was not made until fifty years later, when Dr. R.B. Ellestad provided a chemical analysis for Berg (1938). While Britt reproduces Ellestad's analysis, he interprets it somewhat differently than did Berg, stating that "Except for the presence of minor amounts of magnesia in the samples, these analyses indicate that catlinite is basically the mineral kaolinite with possibly some other similar species (ie., beidellite, montmorillonite) of clay minerals mixed in."

In contrast, Berg (1938: 260) found the Minnesota catlinite to consist predominantly of sericite partially replaced by pyrophyllite. According to him, pyrophyllite has replaced the top and bottom inch of the ca. 15-18 inch bed of catlinite; replacement also occurs along partings parallel to the bedding, in numerous lenses of the massive catlinite, and as scattered specks throughout the body, so numerous that it would be difficult to find as much as a square inch of the red pipestone that did not contain some replacement specks. Berg also noted the presence of diaspore, hematite, specularite, and pyrite. He found most of the diaspore, specularite and pyrite associated with the pyrophyllite replacement. Nearly all of the red hematite, responsible for the color of catlinite, was found in the sericite.

Britt does not reference his statement that catlinite "is basically the mineral kaolinite with possibly other similar species (ie., beidellite, montmorillonite) of clay minerals mixed in," but it does not appear to be correct. Berg's analysis (1938:261) indicates over 5% potash, consistent with his microscopic identification of sericite. X-ray diffraction indicated that the bulk of the catlinite consists of sericite, a form of muscovite mica ("potash mica") generally considered an alteration product of feldspar. In any case, montmorillonite, though abundant in many Mesozoic and Cenozoic sediments, as well as in Recent marine sediments, rarely occurs in sediments older than the Mesozoic (Grim 1953: 356). Beidellite has been found to be a mixture of various clay minerals rather than a distinct mineral, and the term has generally fallen into disuse, following Grim (1953: 40).

In summary, Minnesota pipestone ("catlinite") consists primarily of sericite mica, with diaspore, specularite, and pyrite associated with pyrophyllite replacement. Most of the red hematite, responsible for the color of catlinite, along with small amounts of diaspore and possibly rutile, is found in the sericite. Berg regards the sericite as a product of consolidation or mild metamorphism of the original shale and associated sandstones; the subsequent pyrophyllite replacement may have been a product of hydrothermal alteration. These processes are also reflected in the mineralogy of the overlying Sioux quartzite.

As for Ohio pipestone, twelve chemical analyses have been published by Stout, five of which represent flint clay from the Sciotoville horizon in Scioto Co. (Stout: 129, 131). Stout interpreted the composition of Sciotoville clay as being an impure kaolinite. Noteworthy, in this respect, is the small amount of potassium oxide present; other significant differences when compared with Berg's analysis of Minnesota catlinite are a somewhat greater amount of titanium oxide, suggesting the presence of comparatively more rutile in the Ohio clay, and indication of ancient weathering.

In 1955 de Pablo-Galan presented the results of numerous x-ray diffraction and differential thermal analyses on Ohio clays in his Master's Thesis, where he also presented calculated theoretical mineralogical compositions of the samples. The d.t.a. curves indicated essentially the same minerals for all 35 samples – kaolinite, illite, pyrite, and carbonates. X-ray diffraction confirmed the mineralogy as consisting chiefly of kaolinite, illite, and quartz. De Pablo-Galan included only one sample of Sciotoville clay, and it represented a plastic clay from Stark Co. He calculated the mineral composition of it as 46.10 hydromica (illite) 12.64 kaolinite, 34.32 quartz, 1.30 rutile, 3.37 siderite, 0.23 organic carbon, and 1.16% moisture. De Pablo-Galan cautioned that for a variety of reasons, appreciable error may accumulate in the derivation of such theoretical compositions. Nonetheless, such a composition is consistent with Grim's findings (1953: 358) that Pennsylvanian coal underclays consists of either kaolinite or illite or a mixture of these clay minerals. Such a conclusion was also confirmed by McConnell, Levinson and de Pablo-Galan (1956).

As Holzapfel notes, the Sciotoville clay utilized by prehistoric artisans is a *flint* clay, as opposed to a plastic clay. Grim (1953: 358) defines flint clay as "a dense, hard, nonslakable, massive, non-plastic clay with flint-like characteristics" and notes that the flint clays that had been studied up to that time "are composed of well-crystallized kaolinite in extremely small particle sizes." (The term has nothing to do with the hardness of the rock but refers to its conchoidal fracture, much like that of flint.) Although de Pablo-Galan did not analyze any specimens of Sciotoville flint clay, he did analyze four Ohio flint clay samples from slightly higher stratigraphic units – the Lower Kittanning and Oak Hill members of the Allegheny Group. Study of his analyses indicates that these flint clays have significantly higher amounts of kaolinite – 66.40 to 72.25% than any of the plastic clays analyzed, in keeping with an observation earlier made by Stout (1923: 142) and an interpretation supported by the comparatively small amount of potassium detected in the Ohio flint clays that have been analyzed (including Stout's chemical analyses of Sciotoville flint clay). Further confirmation came from studies of the Kentucky equivalent of the Sciotoville clay – the Olive Hill clay bed (Patterson and Hosterman 1960). Huddle and Patterson (1961) note that in the Pennsylvanian System purer kaolinitic underclays occur in the lower part of the section, whereas illite and mixed-layer clays predominate in younger rocks. They believe that such flint clays were formed by unusually long periods of leaching of acidic seat rock in the substratum of a swamp – leaching which also removed any detrital feldspar (which is more common in plastic underclays). Supporting evidence is the somewhat greater amount of titanium oxide (rutile) in flint clay, as rutile is a stable mineral resistant to weathering. In short, Ohio pipestone (Sciotoville flint clay) probably results from intensively weathered swamp seat-rock and contains more kaolinite than Minnesota pipestone (catlinite), which diagenesis has altered to sericite and pyrophyllite. Whatever the origin of the Minnesota deposits, they appear to have been substantially more altered than Ohio flint clays and mild metamorphism – very likely hydrothermal in part – is a more likely mechanism than simply "the weight of the overlying Sioux Quartzite."

More recent X-ray diffraction studies by Gundersen (1982, 1982a) have been successful in distinguishing Minnesota and Kansan pipestones, in part on the basis of the presence of diaspore and pyrophyllite in the Minnesota pipestone. Sigstad (1973) has used neutron activation analysis to distinguish catlinite and other red pipestones and, in fact, has determined that catlinite from the Hopewellian Esch Mound in Erie County, Ohio, derives from Wisconsin deposits. Sigstad also attributes some catlinite from the Hopewellian Tremper Mound, Scioto County, Ohio, to sources in Minnesota and Arizona. He (Sigstad 1970) has also determined that a simple streak test is sufficient to distinguish Minnesota catlinite from similar materials, including pipestones from Arizona, Kansas, Wisconsin, and Ohio.

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